



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 026 995
A1

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 80303256.4

⑮ Int. Cl.³: **H 01 M 4/96, C 25 B 11/03,**
C 25 B 11/12

⑭ Date of filing: 16.09.80

⑩ Priority: 27.09.79 US 79470

⑯ Applicant: **PROTOTECH COMPANY, 70 Jaconnet Street,**
Newton Highlands Massachusetts (US)

⑪ Date of publication of application: 15.04.81
Bulletin 81/15

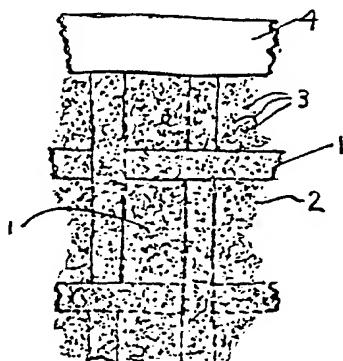
⑰ Inventor: **Lindstrom, Robert, 86 Bond Street, Gloucester**
Massachusetts (US)
Inventor: **Allen, Robert J., 130 Adams Avenue, Saugus**
Massachusetts (US)
Inventor: **Juda, Walter, 12 Moon Hill Road, Lexington**
Massachusetts (US)

⑫ Designated Contracting States: **BE DE FR GB**

⑯ Representative: **Seaborn, George Stephen et al, c/o**
Edward Evans & Co. Chancery House 53-64 Chancery
Lane, London WC2A 1SD (GB)

⑭ Thin carbon-cloth-based electrocatalytic gas diffusion electrodes, processes, and electrochemical cells comprising the same.

⑮ Thin gas diffusion electrodes comprising an open pore carbon cloth substrate [1] provided with a uniform mixture of catalytic carbon particles and preferably Teflon particles [2, 3] adhered within the cloth pores and to the yarns of the cloth; processes for making and using the same; and assemblies comprising said electrodes and closely spaced preferably noble metal current collecting contacts [4] for use in electrochemical cells operating at high current densities.



EP 0 026 995 A1

"Thin Carbon-Cloth-Based Electrocatalytic Gas Diffusion Electrodes, Processes, And Electrochemical Cells Comprising The Same"

FIELD OF THE INVENTION

5 This invention relates to electrocatalytic gas diffusion electrodes and processes for making and using the same; being more particularly directed to thin carbon-cloth-based hydrogen or other ionizable fuel anodes and to air, (oxygen) or other ionizable
10 oxidant cathodes, and to a variety of acid and alkaline electrolyte-containing electrochemical cells embodying the said electrodes, including metal electrowinning cells, caustic-chlorine cells, metal air batteries and fuel cells and the like.

15

BACKGROUND OF THE INVENTION

Gas diffusion electrodes are important tools for converting chemical energy directly and efficiently into electrical energy. In the case of fuel cells, the product is electricity generated by the ionization of hydrogen or other ionizable fuel at an electrocatalytic anode, and by the ionization of oxygen plus water or other ionizable oxidant at an electrocatalytic cathode in an invariant and stationary acid or alkali electrolyte. The currently developing hydrogen - air phosphoric acid fuel cell, for example, consists of many cells of thin hydrogen and air electrodes separated by thin acid-filled matrices, the cells being stacked electrically in series, with current collector plates (designed to allow access of air to one side and hydrogen to the other side) inserted between the cells, and with phosphoric acid electrolyte immobilized within the matrices. In contrast, metal electrowinning cells, as disclosed, for example, in U.S. Patent No. 3,793,165 of common assignee of the present invention and also of

U.S. Patents Nos. 3,262,868 and 3,124,520, utilize a flowing metal-ion-containing electrolyte and a metal cathode in conjunction with a hydrogen anode. In view of the need to remove cathodic metal produced in this 5 type of process, a series connection of cells is usually impractical and, therefore, the current has to be collected from each hydrogen anode. Similarly, air cathodes are advantageous, for example, in chlor-alkali cells and more particularly in such cells 10 comprising ion-exchange membranes wherein substantially chloride free caustic is produced at the cathode, as, for example, also disclosed in said U.S. Patent No. 3,124,520. Here again the caustic catholyte is flowed through the cell and is removed as one product 15 of manufacture. It is, therefore, usually desirable to collect the current from each air cathode. Metal air batteries are other well known cells utilizing air cathodes. Of special interest is the recently proposed aluminium-air battery intended for automotive 20 use, as disclosed in "Metal-Air Batteries for Automotive Propulsion" by J.F. Cooper and E.L. Littauer, submitted to the 13th Intersociety Energy Conversion Conference, 1978. Since, in this application, the 25 battery is to be mechanically recharged by replacing the aluminium anode, and since the anode dissolution product (in this case hydrargellite) is removed periodically, it is again preferable to provide current collection separately from each cathode.

In the cases of fuel cells, batteries and even the 30 copper electrowinning process disclosed in the above-mentioned U.S. Patent No. 3,793,165, electricity is produced either for its own sake or as a by-product of, for example, copper production. In other metal electro-winning, as well as in chlor-alkali production, the 35 electric energy requirement is substantially reduced

by the use of the gas diffusion electrode. Here, part of the electricity is produced in situ from the hydrogen or other active gas (such as sulphur dioxide) fed to the anode, and the air or oxygen fed to the 5 cathode, respectively.

These cells and others comprising gas diffusion electrodes disclosed in the literature have often been held back from commercial application because of the unavailability of sufficiently inexpensive, and well- 10 performing and durable gas diffusion electrodes.

As disclosed, for example, in such standard texts as "Fuel Cell", edited by G.J. Young, Reinhold Publishing Corporation, New York, 1960 and "Fuel Cells", A Review of Government-Sponsored Research, by L.G. Austin, 15 Scientific and Technical Information Division NASA, 1967, and in the patent literature, for example, in U.S. Patents Nos. 3,859,139, 3,912,538 and 4,042,933, known gas diffusion electrodes comprise a gas-porous electrically-conducting substrate which is, typically, 20 either (1) a metallic screen, expanded or porous sintered metal or the like, (2) a thick porous carbon or graphite plate, block or the like, or, more recently, (3) a thin carbon paper.

It is also well known in the prior art that such 25 substrates advantageously carry a uniform mixture of wetproofing binder, preferably fluorinated hydrocarbon polymers, herein referred to as Teflon, with an electrocatalytic particulate noble metal, preferably platinum, uniformly deposited on finely divided high 30 surface area porous carbon carrier particles, as is disclosed for example, in U.S. Patent No. 4,044,193 of common assignee with the present invention.

When air or oxygen electrodes are used in a basic electrolyte (e.g. KOH or NaOH), carbons have long been known to be adequate electrocatalysts in the absence of a noble metal, usually for relatively short term 5 use, as is the case of, for example, some primary metal-air batteries, such as a zinc-air battery.

Thin non-noble metal screens and similar substrates of the prior art, such as nickel or steel screens, are unusable in acid electrolytes as they dissolve therein. 10 Further we have found that such non-noble metals have a serious chemical defect even in aqueous alkaline electrolytes, when they are used in air electrodes comprising the above described catalytic carbon-Teflon particle mixture bonded to the substrate. Oxidation 15 occurs at the interface of the metallic substrate and the catalytic carbon when both are in contact with the alkaline electrolyte and air (or oxygen). This oxidation results either in continuously progressive corrosion of the metallic substrate, as is the case of, 20 for example, steel, or in the formation of an adherent metal oxide coating, such as is the case of, for example, nickel or tantalum. This oxidation constitutes a serious drawback in that it renders the progressively corroding metals, e.g. steel, useless 25 for long-term cell operation; or it increases the electrical resistance of the oxide-coated metals, e.g. nickel and tantalum, lowering electrode performance. It is plausible to attribute this hitherto unrecognized 30 detrimental phenomenon to an electrolytic corrosion current generated by a local shorted non-noble-metal-air (or oxygen) couple. Whatever the explanation, non-noble metallic substrates are clearly undesirable from a corrosion standpoint, in addition to the inherent high cost of thin woven metal screens or 35 sintered metals, relative to the cost of carbons.

Noble metal screen substrates, such as silver screens in alkaline electrolytes, or platinum screens in acid electrolytes, while performing satisfactorily, are usually ruled out because of their excessive cost.

5 In short, metallic substrates are clearly undesirable from a corrosion and/or cost standpoint.

Much of the earlier prior art has focused on porous carbon or graphite which, however, is inherently structurally too weak to be usable in thicknesses much 10 below 1/8". Electrodes based on rigid relatively thick (more than 1/8") porous carbon plate or block substrates have been studied extensively with emphasis on the effect of pore diameter, per cent porosity and gas permeability on electrode performance. Besides 15 being bulky, they are not uniformly porous. Electrodes comprising the same have the catalyst layer usually localized on the face of the plate in contact with the electrolyte to minimize the electrolyte flooding problem. Thus, the gas must be made to diffuse into 20 the other face through a maze of non-uniform tortuous micropores to the catalyst layer, which uneven diffusion lowers electrode performance.

To the contrary, thin porous electrodes are not only 25 advantageous from a weight and volume standpoint, but they permit easy substantially uniform short-path diffusional access of the gas, under minimal pressures, to the active sites of the catalyst layer in contact with the electrolyte.

The relatively recent advent of thin porous carbon 30 paper-based electrodes, as disclosed, for example, in U.S. Patent No. 3,912,538, has overcome the drawbacks of bulk and has shortened the diffusion path. But thin

porous carbon paper substrates are very fragile and they are subject to excessive flooding with electrolyte which interferes with the access of the gas to the electrocatalytic sites of the electrodes. To control
5 the flooding, the carbon papers are often rendered hydrophobic by means of, for example, a Teflon coating which, however, increases their electrical resistivity. In addition, because of their structural weakness, they tend to break in handling as well as in cells operating
10 under moderate gas pressures such as are needed to prevent electrode flooding, particularly when such cells involve a free-flowing electrolyte. Because of their resistivity and fragility, they are supported by a matrix on the electrolyte side, which limits their
15 usefulness, for practical purposes, to stacks of fuel cells, in which the electrolyte is invariant and immobilized within the matrix. Finally, the wet-proofed carbon papers have to be dense to provide a minimum of structural integrity. This characteristic
20 confines the catalytic layer to a surface coating bonded merely to one face of the paper substrate; and being papers, they are inherently non-uniform with respect to porosity.

Surprisingly, we have now found that thin electro-
25 catalytic gas diffusion electrodes comprising substantially uniform open-pore carbon cloth or graphite cloth substrates (hereinafter generically referred to as carbon cloth) of thickness in the range of about 5 to 40 mils, and preferably about 10 to about 35 mils, and
30 a uniform mixture of Teflon or similar wet-proofing particles and catalytic carbon particles embedded and adhered within the cloth pores, have unexpectedly improved electrochemical performance, as well as so much improved structural strength and integrity as to

render them also suitable for use in free-flowing electrolyte-containing electrochemical cells, in contrast to the porous carbon-based electrodes of the prior art. The catalytic carbon particles, as the 5 term is used in this specification and in the appended claims, are either metal-free catalytic carbon particles as later described, or, preferably, porous finely divided high surface area carbons carrying suitable known noble metal catalytic particles, 10 including platinum, palladium, rhodium, iridium, ruthenium and silver, the choice depending on the environment (e.g. acid or alkali, air or hydrogen) and on operating conditions (temperature, current density, intended length of service and others). The platinum- 15 on-carbon described in the above-mentioned U.S. Patent No. 4,044,193 is often the preferred catalyst because of its superior performance and durability. In the special case of an air (oxygen) electrode in an alkaline medium, high surface area porous carbon 20 particles without noble metals are reasonably effective catalysts in and of themselves for oxygen plus water reduction and such and related catalytic carbons are referred to herein as metal-free catalytic carbon particles.

25

SUMMARY OF THE INVENTION

An object of the invention accordingly, is to provide a new and improved thin electrically conducting cloth-based electrocatalytic gas diffusion electrode providing the above and other advantages over previous 30 screen sintered, porous carbon or carbon paper electrodes and the like.

A further object is to provide novel processes for making and using such electrodes, and novel electrode assemblies and electrochemical cells embodying the

same.

Other and further objects will be explained herein-after and are delineated in the appended claims.

In summary, from one of its important aspects, the
5 invention embraces a thin electrocatalytic gas diffusion
electrode comprising an open pore electrically
conducting carbon cloth having a coating of a uniform
mixture of catalytic carbon particles and hydrophobic
binder particles evenly deposited on said cloth, with
10 said mixture of particles adhered within the cloth
pores and to the yarns of the cloth.

In another aspect, the invention provides a process of
preparing an electrocatalytic gas diffusion electrode,
that comprises, uniformly mixing catalytic carbon
15 particles in liquid suspension with hydrophobic
particles; removing liquid and coating the mixture
upon an electrically conducting carbon cloth in such a
manner as to penetrate into the openings of the cloth;
heating the coated cloth to elevated temperature to
20 bind the mixture to the yarns of the cloth and within
the cloth openings; cooling the coated cloth; and
providing current-carrying metallic paths in contact
with said coated cloth.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Embodiments of the invention will now be described by
way of example with reference to the accompanying
drawing wherein;

Fig. 1 of which is an idealized fragmentary view, upon
an enlarged or magnified scale, of a section of the
30 preferred electrode construction of the invention;

Fig. 2 is a graph illustrating the performance of the same;

and Fig. 3 is a longitudinal schematic section of an
5 illustrative cell, illustrated as half of a caustic
cell, embodying the novel electrode of Fig. 1.

BEST MODES OF CARRYING OUT THE INVENTION

Referring to Fig. 1, a suitable substrate in accordance
with the invention is an open pore uniform woven carbon
cloth 1 made by carbonization, at high temperature,
10 of pre-woven carbonaceous fabrics, as described, for
example, in Report No. AFML-TR-77-68 entitled
"Replacement Carbon Fibers for Thermal Protection
Application", by D.L. Schmidt of the Air Force Materials
Laboratories, August, 1977. To provide suitable
15 uniform openings or open pores we prefer a carbon cloth
construction having a warp-to-fill ratio of about unity
($\pm 10\%$), as shown, with between about 25 and 50 yarns
per inch. The carbon content of the cloth should be
in excess of 97% by weight, and preferably at least
20 99% per weight to avoid undesirable impurity interaction
with the electrolyte. We have found that thicknesses
of cloth 1 between 5 and 40 mils are suitable in that
they combine good structural strength with uniformity.
Cloth substrates having thicknesses in excess of 40
25 mils are unnecessarily expensive and begin to be easily
flooded with tenaciously retained electrolyte; and
cloth substrates thinner than 5 mils tend to be
structurally too weak and too deformable.

Carbon cloths of the above preferred characteristics
30 in thickness range of 5-40 mils are now readily
available from commercial suppliers including, among
others, Union Carbide Company and the Stackpole Fibers
Company.

Especially good performance has been obtained with cloths varying in thickness between about 10 and 35 mils, as exemplified in materials sold by the Stackpole Fibers Company under the generic trade name PANEX. By

5 way of specific example, suitable cloth identified as PANEX FWB-3 has the following typical properties:
Construction (warp over fill): 38/38 yarn/inch;
thickness 14 mils.

To prepare an electrode of this invention, a catalytic 10 carbon-Teflon liquid suspension mixture such as, for example, is disclosed in said U.S. Patent No. 4,044,193, is applied to the carbon cloth substrate, as by coating, care being taken to make said mixture penetrate the openings or open pores 1' of the cloth 15 at least partially and sometimes throughout the cloth. The coated cloth is then dried to remove water, and is thereafter heated to a temperature between about 290°C and 350°C for about 3 to about 60 minutes, whereby the catalytic carbon particles 3 and Teflon 20 particles 2 are made to bind together and to adhere to the yarns of the cloth within the cloth pores 1' as shown in Fig. 1.

Surprisingly, thin electrodes of substantially improved 25 electrocatalytic performance and excellent structural strength are thus obtained, in comparison with prior thin carbon paper-based electrodes. Additionally, the cloth-based electrodes are simpler to produce than the paper-based electrodes because the steps of embedding and heating the catalytic carbon-Teflon mixture 3-2 30 within the pores 1' of the cloth 1 results in wet-proofing of the yarns of the cloth, thereby obviating the necessity of rendering the carbon cloth hydrophobic by a Teflon pretreatment, or otherwise, prior to

catalyst application, --a pretreatment usually called for in the case of the carbon paper substrate. While we do not wish to be held to any particular theory, it is plausible to attribute the improved performance 5 of the electrodes of this invention to the uniformity of the catalyst layer evenly embedded within the cloth, to the short diffusion path of the gas to said even catalyst layer; to the more uniform and greater direct exposure of catalyst to the gas; and to the 10 lower electric resistivity of the substrate compared to that to the Teflon-coated hydrophobic paper substrate. The cloth-based electrodes are also somewhat stiffened and are not fragile and retain mechanical stability and electrochemical performance 15 over thousands of operating hours. The catalytic carbon-to-carbon cloth binding involved in this structure moreover, provides the further desirable attribute of similar temperature coefficients of expansion and contraction resulting in mechanical 20 integrity.

Specifically, the preferred electrodes of this invention are made by the methods or processes illustrated in the following examples, it being understood by those skilled in the art that many 25 variations may be made without departing from the scope of the invention, as described in this specification and the appended claims.

Example 1

A platinum-on-carbon sample was prepared substantially 30 in accordance with Example 1, col. 9 of U.S. Patent No. 4,044,193, the pH being adjusted to 3 during the preparation. The air-dried material, containing 9.9% by weight of platinum on Vulcan XC-72 carbon, which

carbon has a surface area of approximately $200 \text{ m}^2/\text{g}$, was compounded with 50% by weight of wet-proofing fluorinated hydrocarbon, herein referred to as Teflon, whereby a typical catalytic carbon-Teflon mixture was 5 formed. The compounding may advantageously use the technique described in commonly owned U.S. Patent No. 4,166,143 (incorporated herein by reference). In this example 1.0 grams of the platinum-on-Vulcan carbon was suspended in 60 ml of distilled water containing 1.4 10 g/l of lanthanum sulphate. The suspension was ultrasonically dispersed and 11.75 ml of the aqueous colloidal Teflon dispersion described in col. 1 lines 35-44 of U.S. Patent No. 4,155,143, containing 85 g/l, was added and the stirring was continued for 5 minutes, 15 whereby the Teflon is completely flocced forming the uniform catalytic carbon-Teflon mixture 3-2. The floc-containing liquid suspension is then filtered, leaving, on the filter, the mixture in a form of a paste suitable for coating the substrate. The coating 20 procedure consisted in applying 0.38 gms of the paste to 9 sq. inches of the above described carbon cloth PANEX PWB-3, the paste being spread uniformly on the surface and into the open pores of the cloth. The coated fabric is then heated to 340°C for about 20 25 minutes. The resulting electrode had a platinum loading of 0.32 mg/cm^2 of electrode area, the platinum being in the form of particles predominantly in the 15-20 Angstrom range.

Note that the term platinum particles, as used herein, 30 refers not only to metallic platinum but also to oxides of platinum which may be formed in the preparation of the high surface area platinum particles.

Example 2

The process of Example 1 was repeated except that the platinum-on-carbon sample was prepared by depositing the platinum-containing sol described in col. 4 of 5 U.S. Patent No. 4,044,193 on Vulcan XC-72, using 225 ml of sol containing 40 gms/l of platinum and 90 gms of Vulcan XC-72. The resulting electrode had a Pt loading of 0.33 mg/cm².

Example 3

10 The method of Example 2 was repeated except that a high surface area carbon known as Norit A, described in the NORIT Bulletin of the American Norit Company of Jacksonville, Florida, 1975, having a surface area of about 900 m²/g, was substituted for the Vulcan XC-72 15 carbon.

Example 4

20 The process of Example 1 was repeated, except that here the Vulcan XC-72 was first partially graphitized by heating to yield a porous carbon having a surface area of about 70-80 m²/g.

25 In general, the porous high surface area carbons suitable for the purposes of this invention are the known porous carbon (including graphitized carbon) catalyst carriers of surface area in excess of about 50 m²/g.

30 In the above examples, there are used the preferred platinum catalyst particles substantially all in the range of 15-25 Angstroms in size. This platinum is preferably prepared from a platinum sulphite complex described, for example, in U.S. Patent No. 4,044,193.

The platinum-on-carbon can be replaced, or used in combination with, palladium-on-carbon, rhodium-on-carbon or ruthenium-on-carbon, the latter three being also formed by oxidation of a complex sulphite of 5 palladium, rhodium and ruthenium, respectively, using, for example, the oxidation technique disclosed in U.S. Patent No. 4,044,193.

These and other noble metals-on-carbon prepared by different known methods are also suitable for the 10 purposes of this invention, though the resultant noble metal catalyst particles are usually less effective than the above described high surface area particles. For example, the known technique of using an aqueous dissolved solution of a silver salt, e.g. silver 15 nitrate, to impregnate a high surface area carbon, followed by evaporation, yields a silver-on-carbon useful as an oxygen reduction electrocatalyst in alkaline media, when applied to the carbon cloth substrate of this invention. A similar iridium-on- 20 carbon can be incorporated in the electrodes of this invention as by the above-described method of making the electrode.

Example 5

A special case is the metal-free catalytic carbon. An 25 air electrode suitable for use in aqueous alkaline media was prepared by the method of Example 1 except that the sample of Vulcan XC-72 carbon, carrying no platinum or other metal, was substituted for the platinum-on-carbon sample.

30 The performance of the gas diffusion electrodes has been measured in a conventional half cell. For example, to evaluate air electrodes in a caustic

(flowing) electrolyte, a vertical half cell of modular construction has been assembled as shown in Fig. 3. On the anode side, a square graphite endplate 5 of dimensions 4-3/4" x 4-3/4" x 1/2", was provided with a 5 small heater pad 6 (2" x 2" x 1/8") mounted in the centre of its outer face. The heater pad 6 provided the means for operating the cell between room temperature and 100°C. A nickel foil anode 7 about 6 mils thick, consisting of a square portion about 10 3" x 3", with two external current collecting tabs 7' (about 3" long and 3/4" wide), was pressed against the centre of the inner face of the graphite endplate 5, and the tabs 7' extended over its upper edge. Under current, oxygen is evolved on the anode. The anode is 15 held in place by several modular components, namely (1) a first of five identical hypalon gaskets 8 (4 3/4" x 4-3/4" x 3/16") having at the centre, a square 2" x 2" opening or "window", which window defines the available electrode area; (2) a first 20 Lucite block 9 (4-3/4" x 4-3/4" x 1") with an opening, 2" wide and 2-1/4" high, matching the window but extending 1/4" above it; (3) a second hypalon gasket 8' with matching window; (4) a thin (1/8") Lucite plate 9' with matching window; (5) the cathode 25 assembly consisting of an air cathode C, later described, 1 (3" x 3" in size), a 6 mil thick nickel foil current collector 4 of the same dimensions as the anode, but having a matching window, the cathode and current collector being sandwiched between a third 30 and fourth hypalon gaskets 8" and 8"'; (6) a second Lucite block 9" (4-3/4" x 4-3/4" x 1/2"), with matching window; (7) a fifth hypalon gasket 8"" with matching window; and, finally, (8) a transparent Lucite endplate 9"" (4-3/4" x 4-3/4") on the cathode 35 side. These modular components were clamped tightly

by means of eight partially Teflon-covered 3/16" stainless-steel bolts 10 with stainless steel nuts, each placed about 3/4" inside the edges of the endplates and about 1-3/4" apart, and traversing the 5 modular components between the endplates.

The opening of the Lucite block 9, which block is provided with electrolyte inlet and outlet tubes 11, is the electrolyte plenum, caustic being continuously pumped therethrough from a reservoir, not shown. The 10 electrolyte plenum is 1/4" higher than the electrode window so that gas, e.g. oxygen, rising to the top, does not reduce available electrode area. Both gas and caustic exit from the top of the plenum, with the caustic returning to the reservoir and the gas vented 15 to the atmosphere. The block 9 is also provided with a thermocouple mounted in a well 12. The Lucite block 9" is provided with air inlets and outlets 13 and its window serves as the air (oxygen) chamber. The transparent Lucite endplate 9'" allows observation 20 of the air chamber and gas side of the cathode 1-2-3.

The same half cell is also suitable for testing of hydrogen anodes. Here, the polarity is reversed, hydrogen is evolved at the now cathodic nickel foil electrode and the diffusion electrode is now anodic 25 and is depolarized by hydrogen.

In a first series of tests the carbon cloth electrode 1-2-3 of Example 1 of the invention was used as the air cathode C in a flowing sodium hydroxide electrolyte containing 23% NaOH. CO₂-free air was fed to the air 30 cathode C and the cathode voltages were measured vs. the Hg/HgO reference electrode (plotted along the ordinate in Fig. 2) as a function of current density

(plotted along the abscissa). The cell temperature was kept at 75°C.

For purposes of comparing performance, a carbon paper-based electrode was also made in accordance with the 5 exact method of Example 1 above, except that a porous carbon paper of the same thickness as the carbon cloth substrate was substituted for the cloth 1. A porous carbon paper, sold under the trade name KUREHA paper (marketed by the Mitsubishi International Corporation, 10 New York, NY) and generally described in United States Patent No. 3,932,197, col. 2, lines 31-32, was used "as is"; that is, without a Teflon pre-treatment which would increase its electric resistivity. The paper-based electrode was then tested on CO₂-free air, 15 again recording cathode potential vs. current density. Fig. 2 and Table 1 show the voltages obtained in the two above-described tests. Comparison of the data obtained with the electrode of Example 1 and the paper-based electrode illustrates the superiority in 20 performance of the cloth-based electrode of the invention.

TABLE 1
Cathode Voltage vs. Hg/HgO Reference

25	Current Density (ASF)	Electrode of Example 1 (Carbon Cloth-based)	Kureha Paper- based Electrode
	10	-0.01	-0.03
	50	-0.08	-0.10
	100	-0.15	-0.17
30	150	-0.21	-0.25
	200	-0.27	-0.33
	250	-0.32	-0.41
	300	-0.39	-0.48
	350	-0.46	-0.57

The larger the absolute magnitude of the voltage, the higher the voltage loss due to polarization of the electrode. It is seen from Fig. 2 and Table 1, that the improvement in performance of the carbon cloth vs.

5 the paper electrode is most pronounced at the high current densities of the order of 250 ASF or more, which are required for economical operation of chlor-alkali cells or metal-air batteries, for example.

10 The overall performance of gas diffusion electrodes, as expressed in cell voltage generation or saving, is not only determined by its electrocatalytic efficiency, but also by other factors. The electron-ion interaction of the electrode reaction occurs on an electrocatalytic site where simultaneous three-phase
15 contact must be effected between the active gas, the solid electrocatalyst and the liquid electrolyte. For the electrode to function under significant current densities, the electrons must be rapidly conducted to or from the catalytic site. With carbon-
20 substrate based electrodes it is known that current collection is a significant factor determining electrode performance.

25 In the case of conducting current from an individual thin carbon cloth-based electrode to an external circuit, contact is made between the electrode and a metallic conductor to the external circuit, as for example, by means of a metal foil window frame 4, Fig. 1, pressed against the rim of the electrode, the window area defining the available or exposed electrode
30 area and the frame having metal tabs which are the contacts to the circuitry. When the metal foil is non-noble metal, such as mickel, it needs to be protected from contact with electrolyte and/or active

gas, for example, by electrically-insulating gaskets made of rubber, plastic or the like. To avoid excessive losses of available or exposed electrode area in arrangements of this kind, the window area 5 should be large relative to the rim area. The electrode itself has to carry electrons from the electrocatalytic sites to the rim, edge or frame. While the combination of carbon cloth and the catalyst layer embedded therein and bonded thereto is 10 surprisingly effective as conductor in cell operation, as compared with the electrical conductivity of the carbon cloth substrate, we have found, however, that there is still an appreciable IR-loss in the thin carbon cloth-based electrode, especially under current 15 densities in excess of about 75 ASF.

Hence, for use in an electrochemical cell operating at high current densities and requiring current collection from individual electrodes, it is often desirable to improve the current carrying capability 20 of the carob cloth-based electrodes. One approach that we have found to be successful in this endeavour is to carry electrons from interior portions of the cloth by metallic conducting paths apart from the carbon cloth and in contact with the same, such as a 25 noble metal screen as of gold-plated nickel, to the current collecting or contact frame.

We have found that the current carrying capability of the carbon cloth-based electrodes can be spectacularly enhanced by current collecting means comprising closely 30 spaced noble metal contacts electrically connected to the electrode. Non-noble metal contacts are not desirable as they suffer from the corrosion effects described above not only in acid, but surprisingly

also in base. With air cathodes in alkaline media, silver is the preferred contact material, as it is the best and lowest-cost conductor among the noble metals. With hydrogen electrodes in metal electrowinning cells, 5 the current collection problem is less severe when these cells are operated at current densities below 75 amps/sq ft, as is usually the case. However, using, for example, electrodes having exposed areas of one square foot or more, improved current collection in 10 acid media is obtained by the use of acid-resistant noble metal contacts, preferably gold contacts.

Other techniques of assembling cloth electrodes and appropriate current collectors will occur to those skilled in the art, being predicated on the principle 15 that the current collecting means comprise closely spaced contacts electrically connected to the electrode, the contacts being made of noble metals and carrying current from interior portions of the carbon cloth electrode to the edge thereof, with contact being 20 enabled with aqueous electrolyte wetting at least about 75% of the exposed area of the electrode and wherein the current collecting means is effectively converted to less than about 25% of said area.

The electrodes and assemblies of this invention are 25 useful in many electrochemical cells including those referred to above. By way of further example, the electrode of Example 1, which has been life tested in the above-described half cell of Fig. 3 over a period of more than one year at a current density of 300 ASF, 30 a temperature of 75°C and with a caustic electrolyte containing 23% NaOH, was also tested in a chlor-alkali cell comprising a NAFION cation-exchange membrane, wherein the cloth electrode was substituted

for the conventional steel cathode. A net voltage gain of .8 volts resulted from the use of the carbon cloth electrode of Example 1 in lieu of the standard steel cathode.

5 It is noted that the half cell test described in this specification has been used in a manner substantially duplicating the operating condition of a typical ion-exchange membrane chlor-alkali cell. The electrode of Example 5 was tested in this half cell and showed a
10 voltage gain of the order of .7 volts vs. the Hg/HgO reference electrode. The performance decay of this noble metal-free electrode with time, however, was more pronounced than that of the electrode of Example 1 in the same environment and under the similar operating conditions.
15

By way of further examples, the electrodes 1-2-3 of Examples 1-4 were tested in a copper electrowinning fuel cell as described in commonly owned U.S. Patent No. 3,793,165 using hydrogen as the fuel, a copper cathode and an aqueous copper sulphate-containing electrolyte. Open cell voltages of between .31 and .33 volts were obtained and, upon substantially shorting the cell, i.e. decreasing the voltage to less than .1 volt, cathodic copper was deposited at current densities ranging between 15 and 20 amps/sq.ft.
20 These same electrodes were also tested in a driven zinc electrowinning cell such as described for example in U.S. Patent No. 3,124,520, embodying a zinc cathode and an aqueous zinc-containing electrolyte, such as zinc sulphate. Here a voltage saving of
25 between 1 and 1.5 volt was noted when the combination of the hydrogen electrode of this invention with associated diaphragm was substituted for the
30

conventional lead anode. Still by way of another example, the electrode 1-2-3 of Example 1 was tested in the aluminium air battery described in the paper entitled "General-Purpose Aluminium-Air/Flywheel

5 Electric Vehicles", by J.F. Cooper and E. Behrin, presented at the Fall meeting of the Electrochemical Society, Pittsburgh, PA, October, 1978 (Paper No. 106). At a current density of 2.5 KAmps/m^2 , this cloth-based electrode 1-2-3 operated at a polarization

10 voltage loss of only 0.2 volts.

The utility of the electrode assemblies of this invention is not limited to the above-named cells, but extends to others including fuel cells, cells generating oxygen from air and the like; and further

15 uses and modifications will occur to those skilled in this art, being considered to fall within the scope of the invention as defined in the appended claims.

CLAIMS

1. A thin electrocatalytic gas diffusion electrode comprising an open pore electrically conducting carbon cloth having a coating of a uniform mixture of catalytic carbon particles and hydrophobic binder particles evenly deposited on said cloth, with said mixture of particles adhered within the cloth pores and to the yarns of the cloth.
5
2. The electrode of claim 1 and in which said catalytic carbon particles comprise catalytic metal particles deposited on high surface area carbon carrier particles.
10
3. The electrode of claim 1 and in which said catalytic carbon particles comprise metal-free catalytic carbon particles.
15
4. The electrode of claim 1 and in which the binder particles are of Teflon.
5. The electrode of claim 4 wherein said cloth has a thickness of between 5 and 40 mils and between about 20 and 50 yarns/inch with a warp-to-fill ratio substantially equal to one, plus or minus 10%.
20
6. The electrode of claim 5 wherein said catalytic carbon particles comprise noble metal particles having been uniformly deposited on high surface area carbon

carrier particles, such noble metals being selected from the group consisting of platinum, palladium, thodium, ruthenium, iridium and silver, and being present in amount between substantially 1% and 25% by weight of said carbon carrier particles and wherein said Teflon is present in amount between substantially 25% and 75% by weight of said mixture.

7. The electrode of claim 6 wherein said noble metal particles are platinum particles substantially in the range of substantially $15\text{\AA} - 25\text{\AA}$ in size and wherein said platinum loads the electrode surface in amount between substantially 0.04 mg/cm^2 and 0.5 mg/cm^2 .

8. A gas diffusion electrode-current collector assembly comprising the electrode of claim 1 and current-collecting means contacting the said electrode.

9. The electrode-current collector assembly of claim 8 and in which said current-collecting means comprises a plurality of metallic current-carrying paths contacting the exposed area of said electrode.

10. The electrode-current collector assembly of claim 9 and in which said current-carrying paths extend from interior portions of said cloth to the edge thereof.

11. The assembly of claim 10 and in which said noble metal is silver.

12. In an electrochemical cell, the assembly of claim 8 in contact with an aqueous electrolyte wetting at least 75% of the exposed area of said electrode and wherein said current-collecting means comprise 5 contacts electrically connected to less than 25% of said area.

13. The cell of claim 12 wherein said electrolyte is free-flowing.

14. The cell of claim 13 wherein said electrolyte 10 comprises concentrated aqueous alkaline hydroxide and said electrode is an air cathode provided with CO_2^- - free air.

15. The cell of claim 8 wherein said electrode is connected as an anode provided with hydrogen.

15 16. The cell of claim 15 wherein the cell is a copper electrowinning cell having a copper cathode in aqueous copper sulphate-containing electrolyte.

20 17. The electrode of claim 1 wherein the electrode is in contact with an aqueous copper sulphate electrolyte and is disposed to diffuse hydrogen therethrough to withdraw copper from the electrolyte.

18. A process of preparing an electrocatalytic gas diffusion electrode, that comprises, uniformly mixing

catalytic carbon particles in liquid suspension with hydrophobic particles; removing liquid and coating the mixture upon an electrically conducting carbon cloth in such a manner as to penetrate into the 5 openings of the cloth; heating the coated cloth to elevated temperature to bind the mixture to the yarns of the cloth and within the cloth openings; cooling the coated cloth; and providing current-carrying metallic paths in contact with said coated cloth.

10 19. A process as claimed in claim 18 and in which the said catalytic carbon particles comprise platinum deposited upon high surface area carbon carrier particles, said hydrophobic particles comprise Teflon in aqueous suspension, and said elevated temperature 15 is of the order of about 290° to 350°C.

20. A process as claimed in claim 18 and in which the current-carrying metallic paths are provided from interior portions of said cloth to the edge thereof.

21. A process as claimed in claim 18 and in which 20 said cloth is stiffened.

22. A process as claimed in claim 18 and in which the cloth is supported at least in part by said metallic paths.

1/2

0026995

FIG. 1

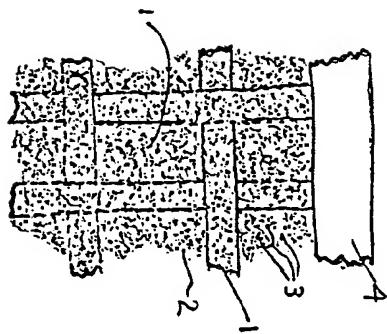
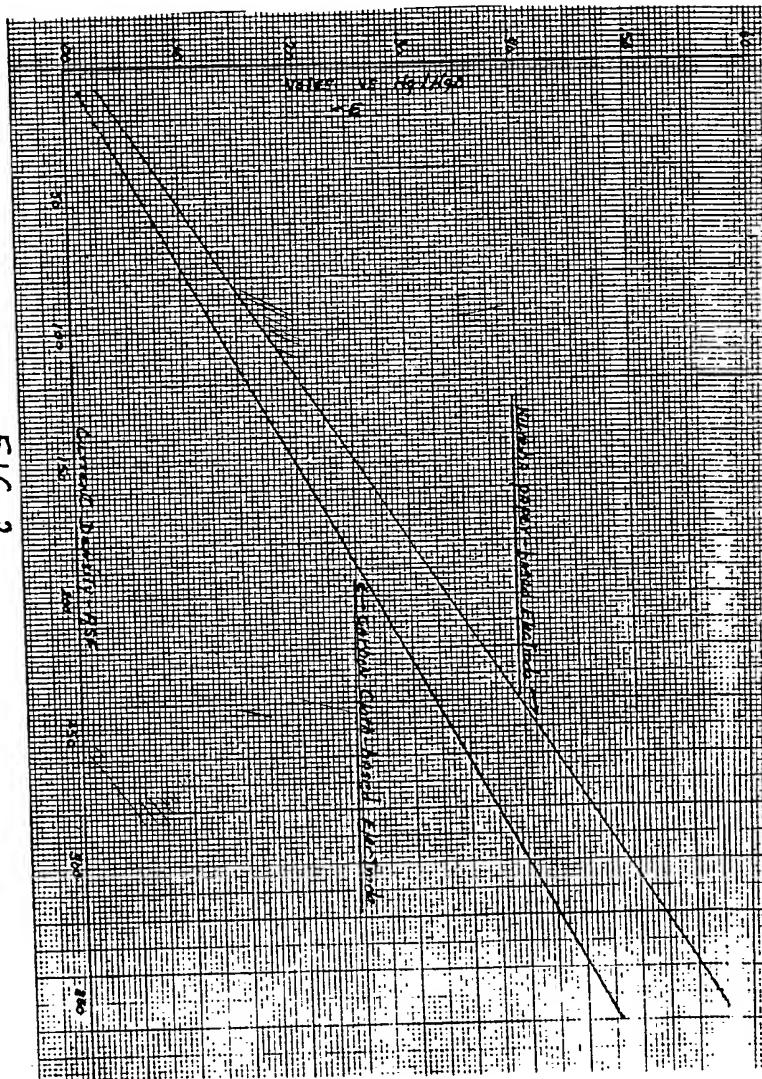


FIG. 2



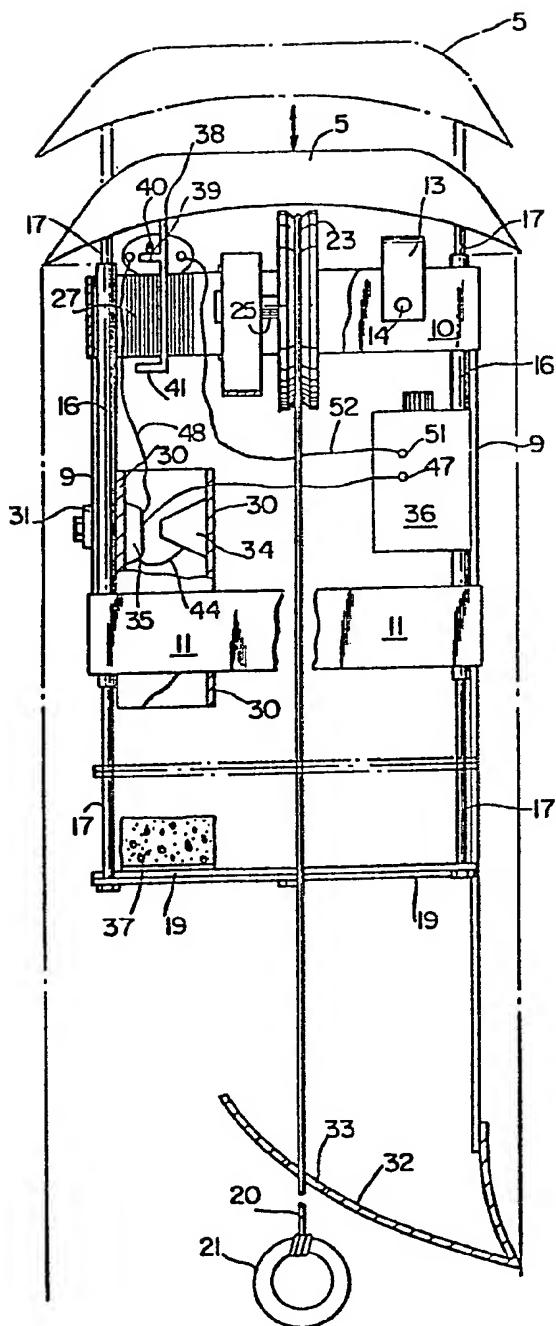


FIG. 3



European Patent
Office

EUROPEAN SEARCH REPORT

0026995

Application number

EP 80 30 3256

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p><u>GB - A - 1 158 580</u> (INSTITUT FR. DU PETROLE)</p> <p>* Claims 1,7,8,10; page 2, lines 12-20, 64-68, 109-112; page 2, line 120 - page 3, line 6, example 2 *</p> <p>--</p>	1,2,4- 7,13- 15,18, 19	H 01 M 4/96 C 25 B 11/03 11/12
X	<p><u>US - A - 3 857 737</u> (F.S. KEMP, M.A. GEORGE)</p> <p>* Column 5, lines 9-44; column 4, lines 17-19,29-31, claim 7 *</p> <p>--</p>	1,2,4, 6,7, 13,18, 19	TECHNICAL FIELDS SEARCHED (Int. Cl.)
X	<p><u>FR - A - 1 599 959</u> (COMP. GEN. D'ELECTRICITE)</p> <p>* Claims A1,2,4,6,8; page 2, lines 38-41; example 2 *</p> <p>--</p>	1,2,4, 8,9, 10,11, 14,20	H 01 M 4/96 4/86 C 25 B 11/03 11/12
	<p><u>FR - A - 2 344 969</u> (ALSTHOM & CIE)</p> <p>* Claims 1,9; page 3, lines 3-30; figure 1 *</p> <p>--</p>	1,2,3, 4,8,9	CATEGORY OF CITED DOCUMENTS
	<u>US - A - 4 058 482</u> (J.M. BARIS, C.D. IACOVANGELO, W.M. VOGEL)	18	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
	* Claim 1, column 5, lines 28-37	*	
D	<p><u>US - A - 4 044 193</u> (H.G. PETROW, R.J. ALLEN)</p> <p>* Claims 1,2,3,8,10,11 *</p> <p>--</p>	7	
A	<p><u>US - A - 3 960 601</u> (D.A. SCHULZ)</p> <p>* Claims 1,5,6; column 11, ./. .</p>	1	&: member of the same patent family, corresponding document
	The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner	
The Hague	14-01-1981	D'HONDT	



European Patent
Office

EUROPEAN SEARCH REPORT

0026995
Application Number

EP 80 30 3256

-2-

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
DA	lines 51-63 * -- US - A - 3 124 520 (W.J. JUDA) * Claims 8,9; example 10 * -----	16,17	